

156/

Polymerizable Derivatives of Long-Chain Fatty Alcohols. III.

Copolymers of Some Alkyl Acrylates and Acrylonitrile¹

EDMUND F. JORDAN JR., WILLIAM E. PALM, and WILLIAM S. PORT, Eastern Regional Research Laboratory,² Philadelphia, Pennsylvania

Copolymers of acrylonitrile containing 5 to 28 mole % (11 to 70 weight %) of three alkyl acrylates (butyl, octyl, and octadecyl) were prepared in *t*-butanol solution. The copolymers were capable of being molded at about 300–400°F. under a pressure of about 2,000 p.s.i. The magnitude of both the tensile strength and the characteristic low temperature of the copolymers varied inversely with the weight percentage of the acrylate present without regard to its alkyl type. The copolymers were oriented with an accompanying three-fold increase in the tensile strength. Good resistance to several selected reagents was shown by all the copolymers.

IT HAS BEEN shown previously that monomers whose homopolymers crystallize provide copolymers with long-chain vinyl monomers (5,10,11,13) which are flexible through a fairly wide temperature range. To some degree these products have approximately the properties of plasticized polymer compositions and have been referred to as "internally plasticized." In general, the deficiencies of the internally plasticized copolymers (particularly of the vinyl chloride copolymers) have been a shorter useful thermal range, greater cold flow, and lower resilience than externally-plasticized polymers. It was reasoned (13) that in the copolymers the distribution of the "plasticizing" comonomer was necessarily random whereas, in the externally-plasticized composition, the plasticizer solvated principally the amorphous regions. The greater retention of crystallinity in the compositions, it was believed, would account for their better properties. A consequence of this reasoning was that modification (through copolymerization) of highly crystalline polymers (such as polyvinylidene chloride) should give products with sufficient retention of crystallinity to show improved properties. It was found that copolymers of vinylidene chloride and octadecyl acrylate (5) did indeed have high resilience. Furthermore it was shown that the long-chain alkyl acrylates were more efficient, both on a molar and on a weight basis, than the short-chain alkyl monomers in lowering the characteristic low temperatures of the copolymers. It was concluded therefore that both a monomer, the homopolymer of which exhibits backbone crystallinity, and a long-chain "plasticizing" monomer were desirable for internal plasticization. Crystallinity, it was believed, was important because the crystallites provided temporary cross-links which would dissolve under stress.

It became of interest to determine whether homopolymers possessing temporary cross-links arising for reasons other than crystallinity could be modified similarly by long-chain monomers. The major source of temporary cross-links in polyacrylonitrile derives

from hydrogen bonding; a minor amount stems from crystallinity. A study was undertaken therefore to determine the effect of alkyl chain-length and of the amount of several alkyl acrylates on the physical properties of their copolymers with acrylonitrile.

The copolymerization of acrylonitrile and alkyl acrylates or methacrylates have been investigated in the determination of monomer reactivity ratios (6,9) in studies of the electrical properties of the copolymers (12) and in research on the elastomeric properties of polyacrylates somewhat modified with acrylonitrile (3). In the present work the interest lies in the physical properties of polyacrylonitrile somewhat modified with alkyl acrylates. The effects anticipated, based on the results of previous work on copolymers of vinylidene chloride (5), were that the use of moderate amounts (about 15 mole %) of an alkyl acrylate would produce internal plasticization and that the long-chain acrylate would be more efficient than the short-chain. The effect sought for in the use of small amounts of the modifying acrylate (about 2.5–5 mole %) was a sufficient lowering of the fusion temperature and of the bulk viscosity to permit the use of the copolymer in hot-melt fiber formation with elimination of the need for solvents.

Preparation of Copolymers. In order to determine the effect of both the alkyl chain-length and of the amount of alkyl acrylate used, a range of copolymers of acrylonitrile were prepared containing about 5 to 30 mole % of, respectively, butyl, octyl, and octadecyl acrylate. The preparation and purification of the acrylate esters were described previously (5). Acrylonitrile, b.p. 77–77.5°C., n_D^{20} 1.3888, was obtained by distilling a commercial grade through a one-foot Widmer column. Copolymerization was carried out in *t*-butanol solution (3 moles per mole of monomer) rather than by emulsion or suspension techniques to avoid problems which might arise from the distribution of acrylonitrile between the aqueous and the organic phases. That such distribution may produce serious effects on the compositional heterogeneity in the copolymers has been demonstrated (4) for the copolymerization of styrene and acrylonitrile. *t*-Butanol was selected as the medium for copolymerization because acrylonitrile has a low transference constant therewith ($C_s = 0.44 \times 10^{-4}$) (1). No attempt was made to control compositional heterogeneity arising from compositional drift with conversion. Previously the monomer reactivity ratios were found to be

$$r_1 = 1.64 \pm 0.04 \text{ and } r_2 = 0.50 \pm 0.19$$

where M_1 is acrylonitrile (6). For the range studied however the copolymer mixture from a given monomer mixture was completely compatible. A small amount (0.025 mole % of the monomers used) of

¹ This paper was presented, in part, at the fall meeting, American Oil Chemists' Society, New York, October 1960.
² Eastern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

dodecyl mercaptan was added as a regulator because some of the copolymers were found to be insoluble when it was omitted. Benzoyl peroxide was used as the initiator in the amount of 0.2 mole % of the monomers (0.3 mole % was used to polymerize the monomer mixture containing 15 mole % octadecyl acrylate and 0.4 mole % for those containing 20–35 mole % of octadecyl acrylate). The copolymers were isolated by pouring the mixture of copolymers and t-butanol into five volumes of methanol. Unused monomers were removed by three extractions with hot methanol, and the copolymers were dried to constant weight. Table I lists the compositions of the monomer mixes used, the percentage of conversion to copolymer, and the composition of the copolymers obtained.

Physical Properties of the Copolymers. The principal criteria for the evaluation of the physical properties of the copolymers were the yield tensile strength and the characteristic low temperature as measured in the Clash and Berg (2) apparatus (the temperature at which the torsional modulus is 135,000 p.s.i.). Samples for testing were molded in a press at 2,000 p.s.i. or were films cast from solution. The casting solutions contained 5–10% of the copolymer, and the solvent used was dimethylformamide or a 1:1 solution of dimethylformamide and benzene. The molding temperatures are given in Table I.

TABLE I
Compositions and Physical Properties of Copolymers,
of Acrylonitrile and Alkyl Acrylates

Acrylate in Monomer Mix.		Con- version %	Acrylate in Copolymer		Molded Specimens			Cast Specimen— yield tensile p.s.i.
Mole %	Weight %		Mole %	Weight %	Clash- Berg Tr°C.	Yield tensile p.s.i.	Mold- ing temp., °F.	
Butyl Acrylate								
5	11.3	84	4.9	11.0	75	400	11,700
15	29.9	78	11.4	23.7	65	10,500	400
20	37.6	77	14.7	29.4	54	290
30	50.8	71	21.8	40.3	38	6,000	290
35	56.6	69	26.1	46.1	28	4,200	290	4,550
Octyl Acrylate								
5	16.0	69	4.0	12.5	83	410	11,700
10	27.8	71	7.2	21.2	69	410	9,200
15	38.0	60	9.5	26.6	59	7,850	400	8,900
20	46.5	58	12.5	33.3	52	7,300	400	8,200
25	53.6	37	14.5	37.1	46	6,800	360	7,050
30	59.8	68	22.7	50.5	26	3,700	360	4,000
Octadecyl Acrylate								
5	24.3	84	4.3	21.5	64	400	10,200
15	51.8	81	12.5	46.6	26	3,700	380	4,500
20	60.7	83	16.6	54.9	12	2,700	340	2,800
30	72.4	66	22.8	64.3	—5	2,000	310	2,700
35	76.7	77	28.0	70.4	—15	2,100	310

The table also lists the characteristic low temperatures and the tensile strength at the yield-point of the copolymers prepared. The magnitude of both properties decreases as the alkyl acrylate content increases. As Figure 1 shows, there is a marked dependency of the characteristic low temperature and of the tensile strength on the weight percentage of the alkyl acrylate irrespective of the length of the alkyl chain. (The data for tensile strength used in the figure are for the cast film or, when not available, for the molded specimen.) This dependency is in striking contrast with the effect of the alkyl chain-length in copolymers of vinylidene chloride and alkyl acrylates (4) where the alkyl chain-length had an important effect. Mandelkern and Flory and others (8) have shown that, in compositions of polymers and diluents, there is a

simple dependence of the second-order transition temperature and the volume fraction of the diluent. Therefore, since the weight and volume fractions are closely related, the alkyl acrylate in the present copolymers are probably behaving simply as diluents. All the copolymers had low elongations at yield (10% or lower).

Attempts were made to orient both the cast and molded specimens, using the Instron tensile tester. The samples were heated to 60°C. and stretched 300

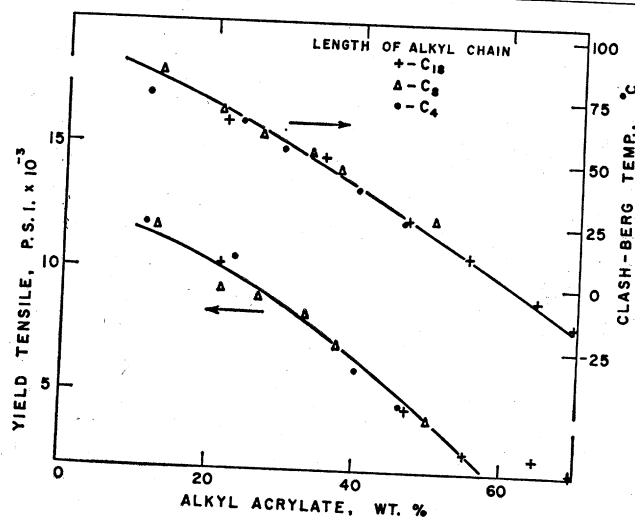


Fig. 1. Variation of yield tensile strength of Clash-Berg temperature of copolymers of acrylonitrile with alkyl acrylate contents.

to 1,000% at the rate of 0.2 in. per minute. The tensile strength was thereby increased approximately three-fold. An x-ray diffraction study of the unstretched and stretched films revealed that orientation of the polymer backbone was only slight. Representative copolymers containing octadecyl acrylate showed scattering maxima at 5.3 and 4.3 Å, which are characteristic of polyacrylonitrile and poly(octadecyl acrylate), respectively. Therefore it is probable that the octadecyl acrylate segments and the acrylonitrile backbone segments crystallized separately. This behavior is similar to the separate crystallization found in copolymers of vinyl alcohol and vinyl stearate (7).

Resistance to Chemical Reagents. Because a possible use for copolymers of acrylonitrile and alkyl acrylates lies in the field of laminations, tests were made to determine their resistance to selected chemical reagents. Samples were immersed at room temperature in soybean oil, 50% alcohol, 1% sodium hydroxide, and 3% and 30% sulfuric acid. The percentage increases in weight were determined after 160 hrs. of immersion. The increase in weight was less than 1% for all samples for all the reagents except 50% alcohol. In the latter the weight percentage increase varied from 1 to 3%, increasing with acrylate content and decreasing with the alkyl chain length of the acrylate. The use of a long-chain acrylate thus imparts slightly greater chemical resistance to the acrylonitrile copolymer.

Acknowledgment

The authors thank Lee P. Witnauer for valuable discussions on the physical properties reported.

REFERENCES

1. Chatterjee, D., and Palit, S.N., Proc. Roy. Soc. (London), A227, 252 (1955).
2. Clash, R.F. Jr., and Berg, R.M., Modern Plastics, 21, No. 11, 119 (1944).
3. Dietz, T.J., and Hansen, J.E., Rubber Age, 68, 699 (1951); Filachione, E.M., Fitzpatrick, T.J., Rehberg, C.E., Woodward, C.F., Palm, W.E., and Hansen, J.E., *ibid.*, 72, 631 (1953); Hansen, J.E., and Palm, W.E., *ibid.*, 75, 677 (1954).
4. Fordyce, R.G., and Chapin, E.C., J. Am. Chem. Soc., 69, 581 (1947); Fordyce, R.G., *ibid.*, 69, 1903 (1947); Smith W.V., *ibid.*, 70, 2177 (1948); Mino, G., J. Polymer Sci., 22, 369 (1956).
5. Jordan, E.F. Jr., Palm, W.E., Witnauer, L.P., and Port, W.S., Ind. Eng. Chem., 49, 1695 (1957).
6. Jordan, E.F. Jr., Doughty, K.M., and Port, W.S., J. Applied Polymer Sci., 4, 203 (1960).
7. Jordan, E.F. Jr., Palm, W.E., Swern, Daniel, Witnauer, L.P., and Port, W.S., J. Polymer Sci., 32, 33 (1958).
8. Mandelkern, L., and Flory, P.J., J. Am. Chem. Soc., 73, 3210 (1951); Fox, T.G., Phys. Rev., 86, 652 (1952); Boyer, R.F., J. Appl. Phys., 22, 723 (1951); 25, 825 (1954).
9. Marvel, C.S., and Schwen, R., J. Am. Chem. Soc., 79, 6003 (1957); Okamura, S., and Yamashita, J., J. Soc. Textile and Cellulose Ind., Japan, 9, 444 (1953); [C.A. 48, 1010b (1954)]; Tamikado, T., and Iwakura, Y., J. Polymer Sci., 36, 173 (1959).
10. Port, W.S., Jordan, E.F. Jr., Palm, W.E., Witnauer, L.P., Hansen, J.E., and Swern, Daniel, U.S.D.A., Agricultural Research Service, A.I.C., 366 (1953).
11. Port, W.S., Jordan, E.F. Jr., Palm, W.E., Witnauer, L.P., Hansen, J.E., and Swern, Daniel, Ind. Eng. Chem., 47, 472 (1955).
12. Rosenberg, J., and Greenberg, H.L., Modern Plastics, 35, No. 4, 173 (1957).
13. Silbert, L.S., Jacobs, Z.B., Palm, W.E., Witnauer, L.P., Port, W.S., and Swern, Daniel, J. Polymer Sci., 21, 161 (1956).

[Received August 8, 1960]